

# Biosorption of heavy metals and radionuclide from aqueous solutions by pre-treated arca shell biomass

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## Abstract

In this study biosorption potential of pre-treated arca shell biomass for lead, copper, nickel, cobalt and cesium was explored from the artificially prepared solution containing known amount of metals. The effects of pH, initial concentration, biosorbent dosage and contact time were studied in batch experiments. Effects of common ions like sodium, potassium, calcium and magnesium on the sorption capacity of pre-treated arca biomasses were also studied. To analyse the homogeneity of the biomaterial, experiments were performed for eight lots arca shell biomass for all the studied elements and it was observed that relative standard deviation in uptake capacity was within 10% for all elements. At equilibrium, the maximum total uptake by shell biomaterial was  $18.33 \pm 0.44$ ,  $17.64 \pm 0.31$ ,  $9.86 \pm 0.17$ ,  $3.93 \pm 0.11$  and  $7.82 \pm 0.36$  mg/g for lead, copper, nickel, cesium and cobalt, respectively, under the optimised condition of pH, initial concentration, biosorbent dose and contact time. Effect of all the common ions jointly up to concentration of 50 ppm was negligible for all the elements but at higher levels the cations affects the uptake capacity. Sorption isotherms were studied to explain the removal mechanism of both elements by fitting isotherms data into Lagergren, Freundlich and Langmuir equations. Halls separation factor estimated under optimised condition also favours the sorption potential of these elements using arca shell biomass. Arca shell biomass can be effectively and efficiently employed for removal of studied elements after optimisation of parameters.

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**Keywords:** Copper; Lead; Nickel; Cesium; Cobalt; Lagergren; Langmuir; Freundlich isotherm

## 1. Introduction

Industrial effluents are the byproduct of industrialisation gets attention of environmental scientist and engineers to deal with problem of water pollution. Water pollution is one of the most debatable as almost all inorganic or organic wastes are discharged through aquatic route either in water soluble or insoluble forms. The presence of heavy metals in the aquatic system has been become a great concern for local environment and public residing in the vicinity, because of their toxicity, their accumulative poisonous effects capable of being assimilated, accumulation in food chain, persistence in nature and concentrated by organisms in various part of biosphere. Copper released to aquatic system affects some of the varieties of oysters, it makes complexes with carboxylic acid present in their body and turns them green and become unmarketable. Lead affects the

soil microorganism by retarding the heterotrophic breakdown of organic matter [1,2]. Stable cesium ( $^{133}\text{Cs}$ ), is the rarest of the alkali metals, has little economic value and no essential biological role. However, nuclear technology has resulted in release of radioactive isotopes of cesium into environment.  $^{137}\text{Cs}$  is one of the most abundant radionuclides in the nuclear fission having long radiological half-life (30 years) [3–5]. Its metabolic similarities to potassium favour its uptake and accumulation by plants after radio-contamination of water body and ultimately agricultural field. It enters into many food chain pathways to cause radiation exposure to human being and other ecological biota of the ecosystem [6]. Nickel at trace amount may be beneficial as an activator of some enzyme systems [7]. At higher levels, it accumulates in the lungs and may cause bronchial hemorrhage, nausea, weakness and dizziness. However, nickel compounds are not currently regarded as either human or animal carcinogens [8], but the possibility that Ni can act as a promoter has been reported [9]. Cobalt is widely used and dispersed in the environment due to human activities in all the parts of biosphere from mining, processing and its uses. It is beneficial for human

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Table 1  
Advantages and disadvantages of conventional metal removal technologies

Method	Disadvantages	Advantages
Chemical precipitation and filtration	At higher concentrations difficult separation; not effective and resulting sludges	Simple and cost effective
Chemical oxidation or reduction	Chemical required, biological systems are very slow and climate sensitive	Mineralisation
Electrochemical treatment	At higher concentration very expensive	Metal recovery
Reverse osmosis	High pressures and membrane scaling; very expensive	Quality of effluent for recycling the water
Ion exchange	Sensitive to particles; Expensive resins	Effective, pure effluent and metal recovery
Adsorption	Not that viable for metals	Conventional adsorbent (carbons)
Evaporation	Energy intensive, resulting sludges and very expensive	Quality of effluent for recycling the water

Ref. [61].

being as it is a part of vitamin B<sub>12</sub>, which is highly essential for human health. Cobalt supplements are also given in medicines to the patients suffering with anemia. But at higher level cobalt may affect human health. When the plants are grown on the soil having higher amount of cobalt or irrigated with water having its elevated concentration, it gets accumulated in the plants and enters in the food chain. Higher intake of cobalt can cause vomiting, nausea, vision problem, heart problem, and thyroid damage.

Once these trace metals or radionuclides are released in the environment it would be a herculean task to get rid of these contaminants from the food chain. It is very necessary to remove these at the time of release of effluent. There are some conventional methods for treatment of liquid effluent for removal of traces of heavy metals such as ion exchange, chemical precipitation, reverse osmosis, coagulation and co-precipitation, have been designed to remove radionuclides and metal ions from the effluents having their respective advantage and disadvantages are listed in Table 1.

During past few decades biosorption process has been studied extensively using various biomasses to achieve the goal in field of heavy metal removal from aquatic effluent using low cost bio-materials as adsorbents. It has been revealed from the detailed review of literature available that a large number of researcher are working on various cheaper biomaterials like raw rice bran [10], rice husk [11], alga *Chlorella vulgaris* [12], marine green alga *Ulva reticulata* [13], eggshells [14], dried activated sludge [15], *Mucor hiemalis* [16], olive pomace [17], crushed coconut shell and treated saw dust [18], peanut hull [19], bagasse pith biomass and saw dust [20], cork and yohimbe bark [21], granular kohlrabi peel [22], papaya wood [23], coir (fibres from *Coco nucifera*) [24], marine algae *Ulva fasciata* and *Sargassum* sp. [25], sugarcane dust [26], crab shell particles [27], cone biomass of *Pinus sylvestris* [28], *Aspergillus flavus* biomass [29], *Moringa oleifera* seeds [30], powdered waste sludge [31], Eucalyptus bark [32], sugarcane bagasse carbon [33–34] and marine algae biomass and treated mangrove root biomass [35,36] as sorbents for heavy metal removal from aquatic effluents. The sorption of cobalt and cesium has been studied by using an agro-based mucilaginous seeds [37]. Sorption behaviour of uranium and thorium has been studied by agro-based biomass as well [38]. In some other studies removal abilities of various biosorbents like sorghum straw, flyash, banana pith, Charoli

bark, bacteria, algae, fungi and yeast dead biomass and various viable species were also investigated [39]. Waste and low cost biomasses from terrestrial environment are studied at large scale for biosorption of heavy metals, dyes, etc. all over the world. But, a few reports are available on exploration of biosorption potential of marine biomasses. Keeping in view the above discussed problem and easy availability of arca shell biomass from the fishing industry, an attempt is made to investigate the scope of biosorption capacity of this material for removal of lead, copper, nickel, cobalt and cesium from simulated aqueous solutions.

## 2. Material and method

### 2.1. Chemical reagents and instrumentation

All the chemicals used were of analytical grade. Stock solution were prepared from CuSO<sub>4</sub>·5H<sub>2</sub>O for copper and from Pb(NO<sub>3</sub>)<sub>2</sub> for lead and CsCl salt for cesium, Co(NO<sub>3</sub>)<sub>2</sub> for cobalt, NiSO<sub>6</sub>·H<sub>2</sub>O for nickel using demineralised water from Millipore Elix-3. Millipore demineralised water was used for all the further dilution wherever needed during this study. Stock solution of 10,000 ppm was prepared, which was used as stock standard solutions for entire study. The required dilutions were made from stock solution to desired concentration using deionized water from Millipore Elix-3. All the chemicals used were A.R./Electronic grade. Millipore demineralised water was used for all the further dilution wherever needed during this study.

Elico-120SL pH meter was used for measurement of pH while adjusting the pH of the solutions using 0.1N NH<sub>4</sub>OH/0.1N HNO<sub>3</sub>. The concentration of the solution before and after sorption was measured by using flame (air/C<sub>2</sub>H<sub>2</sub>) atomic absorption spectrometer (Model GBC, Avanta PM) with background correction using deuterium lamp for all the four elements except cesium. All the measurements were made under optimised conditions of the parameters given in Table 2. Cesium estimation was done indirectly by spiking the solution with known amount of radioactive tracer (<sup>137</sup>Cs). Samples were counted before and after sorption by gamma spectrometer using NaI(Tl) detector. As radioactive and stable isotopes of cesium are chemically similar, exchange was estimated from the amount of radioactive counterpart removed from initial quantity. Samples containing <sup>137</sup>Cs were counted on NaI (Tl) based scintillation  $\gamma$ -ray spectrometer. The detector used was 4 in.  $\times$  4 in. well type detec-

Table 2  
Optimised conditions used for analysis of lead and copper during the study

Element	Lamp current (mA)	Wavelength (nm)	Bandwidth (nm)	Range ( $\mu\text{g/mL}$ )	Detection sensitivity ( $\mu\text{g/mL}$ )
Cu	3.0	222.6	1.0	45–180	1.0
Pb	5.0	283.3	0.5	7.0–50.0	0.16
Ni	4.0	232.0	0.2	1.7–8	0.04
Co	6.0	240.7	0.2	2.5–9	0.05

tor (MAKE BICRON, USA). The well dimension was 1 in. diameter and 2.25 in. height. The output of the detector was coupled to 1 K multichannel analyzer (PC based) for data analysis. The net area of the photo peak was calculated by subtracting Compton continuum. Typical counting time selected was 60 s.

## 2.2. Experimental and kinetics model

Arca shell biomasses used in this study were collected from fishermen of Trombay village. Organism shells were separated from the meat by boiling. A total of eight lots of arca shell were collected separately and processed separately as well. These were washed with tap water followed double washing with distilled water to remove any soluble if present on their surface. After drying these were grounded and sieved through Jayant Test Sieves No. 30 (ASTM) to separate particles having size more than 600  $\mu\text{m}$ . Sieved material was used for sorption studies.

For optimisation of pH, contact time and sorbent dose and initial concentration, batch sorption experiments were performed at room temperature ( $25 \pm 2^\circ\text{C}$ ). Sorption experiments for lead, copper, nickel, cesium and cobalt metals were conducted in the pH range of 1–7, sorbent dosage 0.1–15.0 g/L, initial concentration from 10 to 500 ppm and contact time from 10 min to 7 h. In case of sorption studies of cesium 100 mL solution of the solution having known amount of stable cesium was spiked with 260 Bq of  $^{137}\text{Cs}$ . pH of the solution was adjusted by using 0.1N  $\text{NH}_4\text{OH}/0.1\text{N HNO}_3$ . Effect of competitive ion was also studied after addition of different concentrations of sodium, potassium, calcium and magnesium separately and in the combinations of sodium + potassium, calcium + magnesium and calcium + magnesium + sodium + potassium at different concentrations 10, 20, 50, 100, 200 and 500 ppm. Kinetic isotherms of sorption data were studied at varying concentration from 10 to 500  $\mu\text{g/mL}$  of initial concentration using optimised dose of ASB for all the studied elements under optimised condition of pH and contact time. All the experiments were done in triplicate and means of all the three are reported. Aliquots of the treated samples were filtered using ash-less and fine crystalline filter paper Whatman No. 42 and filtrate were analysed for respective element.

### 2.2.1. Metal uptake

Preliminary experiments had shown that metals adsorption losses to the flask walls and to the filter paper were negligible. The results were expressed as the amount of copper ions adsorbed on dried algae at experimental equilibrium and the

concentration of copper ions that remain in solution at the equilibrium. The metal uptake was calculated by the simple concentration difference method [40].

### 2.2.2. Kinetics isotherm

Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimising operating procedures [41].

### 2.2.3. Lagergren model

Two different kinetic models were used to adjust the experimental data of metal biosorption on ASB. The pseudo first-order Lagergren model is generally expressed as:

$$\frac{dq}{dt} = K_L(q_e - q_t) \quad (1)$$

where  $q_e$  (mg/g) and  $q_t$  are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time  $t$ , respectively, and  $K_L$  is the Lagergren rate constant of the first-order biosorption. Integrating (Eq. (1)) between the limits,  $t = 0$  and  $t$  and  $q = 0$  and  $q_e$ , it becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303}t \quad (2)$$

Linear plots of  $\log(q_e - q)$  versus  $t$  indicate the applicability of this kinetic model.

### 2.2.4. Langmuir and Freundlich isotherm model

To examine the relationship between sorbed ( $q_e$ ) and aqueous concentrations ( $C_e$ ) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data, initial metals concentrations were varied while the biomass weight in each sample was kept constant. The Langmuir model assumes the form:

$$q_e = \frac{abC_e}{1 + bC_e} \quad (3)$$

where  $a$  (mg/g) is the maximum amount of metal ion per unit mass of arca shell biomass to form a complete monolayer on the surface and  $b$  is the equilibrium adsorption constant which is related to the affinity of the binding sites.  $a$  represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and allows the comparison of adsorption performance, particularly in the cases where the sorbent did not reach its full saturation in experiments [42]. The Langmuir parameters

can be determined from a linearized form of Eq. (3), represented by:

$$\frac{C_e}{q_e} = \left( \frac{C_e}{a} \right) + \frac{1}{ab} \quad (4)$$

According to Eq. (6), a plot of  $C_e/q_e$  versus  $C_e$  gives a straight line with slope of  $1/a$ , and intercept is  $1/(ab)$ .  $b$  can be related to the adsorption free energy,  $\Delta G_{\text{ads}}^\circ$ , by the following equation [11,32,43,44].

$$\Delta G^\circ = -RT \ln K \quad (5)$$

where  $\Delta G^\circ$  is the change in free energy (J/mol),  $R$  the universal gas constant = 8.314 J/K mol,  $T$  the absolute temperature (K), and  $K$  is the equilibrium constant at temperature  $T$ .

The equilibrium constant,  $K$  can be calculated from:

$$K = \frac{q_e}{C_e} \quad (6)$$

where  $q_e$  and  $C_e$  were same as mentioned above in Eq. (4).

The Langmuir constant can be used to determine the suitability of the adsorbent to adsorbate by using dimensionless parameter, Hall separation factor ( $R_L$ ), which is defined as

$$R_L = \left( \frac{1}{1 + bC_0} \right) \quad (7)$$

$R_L$  was calculated for both the elements sorption on both biomasses at 100  $\mu\text{g/mL}$  initial concentration and values are given in Table 3, where  $b$  is Langmuir constant (L/mg) and  $C_0$  is the initial concentration (mg/L).  $R_L$  is also known as the constant separation factor or equilibrium parameter [45]. The slope of the linearized Langmuir isotherm can be used to interpret the type of sorption using the value of  $R_L$  as follows:

$R_L < 0$ ,	unfavourable;
$R_L > 1$ ,	unfavourable;
$R_L = 1$ ,	favourable;
$0 < R_L < 1$ ,	favourable;
$R_L = 0$ ,	irreversible.

Table 3

Coefficient for Lagergren, Langmuir and Freundlich isotherm for arca shell biomass for all the studied elements

Isotherm	Coefficient	Lead	Copper	Nickel	Cesium	Cobalt
Langmuir	$a$	30.39	26.88	11.75	4.76	11.53
	$b$	0.069	0.059	0.281	0.228	0.225
	$R^2$	0.985	0.979	0.992	0.997	0.984
	$R_L$	0.125	0.146	0.034	0.082	0.043
	$\Delta G_{\text{ads}}$ (kJ mol <sup>-1</sup> )	-19.1	-18.11	-21.99	-10.99	-20.26
Freundlich	$K_F$	4.848	3.977	3.538	1.946	2.853
	$1/n$	0.353	0.362	0.253	0.174	0.251
	$R^2$	0.828	0.863	0.725	0.733	0.921
Lagergren	$q_e$	18.63	22.66	12.97	5.175	11.36
	$K_L$	0.013	0.012	0.011	0.017	0.026
	$R^2$	0.976	0.978	0.957	0.986	0.952

### 2.2.5. Freundlich equation

Freundlich equation is used for heterogeneous surface energy term. The Freundlich equation is widely used in the environmental engineering practice to model adsorption of pollutants from an aqueous medium empirically. Freundlich isotherm can also be used to explain adsorption phenomenon as given below.

$$q_e = K_F C_e^{1/n} \quad (8)$$

The linearized Freundlich model isotherm is represented by equation

$$\log_{10} q_e = \log_{10} K_f + \frac{1}{n} \log_{10} C_e \quad (9)$$

where  $K_f$  and  $n$  are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto carbon, respectively.

According to Treybal [60], mathematical calculations have shown that  $1/n$  values between 0.1 and 1.0 correspond to beneficial adsorption. The plots of  $q_e$  versus  $C_e$  in log scale can be plotted to determine values of  $1/n$  and  $K_f$  from power equation depicting the constants of Freundlich model.

## 3. Result and discussion

### 3.1. Homogeneity of biomass

Arca shell were collected in eight lots and processed separately. From each lot 0.5 g of biomaterial was equilibrated with same initial concentration of all the studied elements under optimised condition of pH and contact time. The relative standard deviation for metal uptake capacity of ASB was 8.2, 9.6, 5.0, 9.0 and 4.4 for lead, copper, nickel, cesium and cobalt, respectively. This shows that biomaterial is homogeneous and biomass from all of these lots were mixed and used for the entire study.

### 3.2. Sorption of lead, copper, nickel, cobalt and cesium on arca shell biomass

#### 3.2.1. Effect of pH

Sorption potential of biosorbent over the experimental range of 1–7 for all the five elements. In case of lead the optimised condition for sorption were observed at pH 4.0 (Fig. 1). Uptake

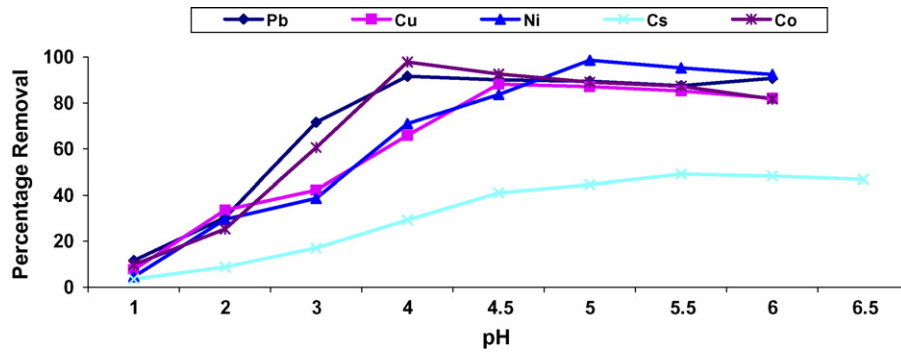


Fig. 1. Effect of pH on percent removal of all the studied elements using chemically arca shell biomass.

of lead increases from 2.3 mg/g at pH 1 to 18.33 mg/g at pH 4 and at higher pH the uptake decline as well. At higher pH lead precipitated out from the solution as its hydroxides. In case of copper the percentage removal was increased from 1.54% at pH 1 to 88.2% at pH 4.5 and at higher pH it remains almost constant with little decrease. Nickel removal was observed maximum at pH 5 with a 98.6% removal which was less than 30% in the range of pH 1–3 (Fig. 1). At low pH protons would compete with metal ions for active binding sites. Optimum cesium removal was observed at pH 5.5 using arca shell biomass. The percentage removal was observed 98.2% at pH 5.5, which was less than 35% below pH 3 (Fig. 1). Cobalt removal was increased from 9.8% at pH 1 to 97.8% at pH 4 and decline at higher pH as well (Fig. 1). At low pH in the range from 1 to 3 almost all the binding sites may be protonated, may be responsible for low sorption capacities [46,47].

### 3.2.2. Effect of contact time

The lead removal more than 50% was observed within first 60 min, even there was an increase in the uptake of the lead up to the contact time of 240 min considered as optimised (Fig. 2). Approximately 91.66% of total uptake capacity of lead from the solution was sorbed in 4 h contact time and after that there is no appreciable change. Hence for rest of the study the optimised contact time for all experiment was taken 4 h. In case of copper just 30% removals was observed in first hour, which increases to a level of 88.1% after 5 h (Fig. 2). In rest of the experimental work 5 h contact time was taken as optimised for copper removal by arca shell biomass. In case of nickel removal with contact time follow the same trend as was observed in case of

copper. In first 1 h the removal was just 28% which increases to 98.6% in duration of 5 h (Fig. 2). In case of cesium removal the sorption is rapid than copper and nickel may be due to the mono valency of cesium. A removal of 46% was observed with in first 60 min with an optimum contact time of 3 h having 98.2% removal (Fig. 2). Even though the optimum contact time for cobalt removal was also observed as 3 h with a 97% removal, but in this case more than 60% sorption potential was observed with first hour and thereafter a slight increase was observed. The rapid initial sorption was likely due to extra-cellular binding and the slower sorption likely resulted from intracellular binding [48]. Uptake variation with time for all the studied elements using arca shell biomass was used in fitting of Lagergren isotherms shown in Fig. 3.

### 3.2.3. Effect of biosorbent dose rate

Sorption behaviour of biosorbent at different dosages from 0.1 to 12.5 g/L have been studied in 100 µg/mL of solution under optimised condition of pH and contact time for all the elements except cesium where the optimum initial concentration was observed as 50 ppm. Variation in the uptake of all elements per gram of biomaterial dosage rate decreases with increases with the dosage rate. At a dosage more than 5.0 g/L there is a decrease in the uptake but at very low dosage total amount of lead and copper removal in very less, which indicates the high residual concentration. For the rest of the study 5.0 g/L dosages is considered as optimum dosage for lead and copper removal. In case of nickel the optimum dose on the basis of uptake of metal per gram and the residual concentration in the treated solution was observed at 10.0 g/L. But for cobalt and cesium removal

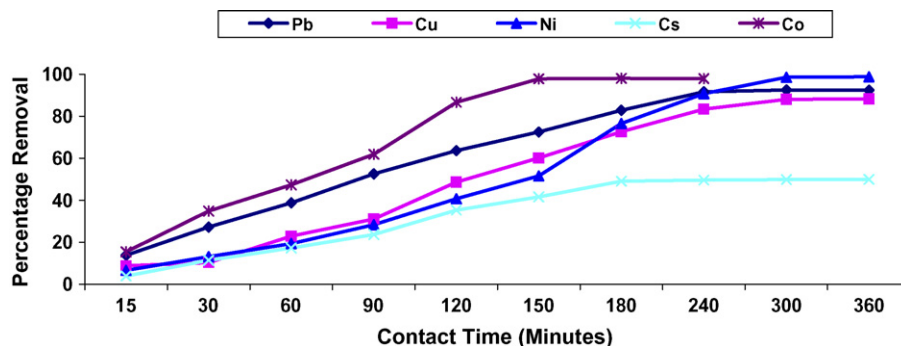


Fig. 2. Effect of contact time on percent removal of all the studied elements using arca shell biomass.



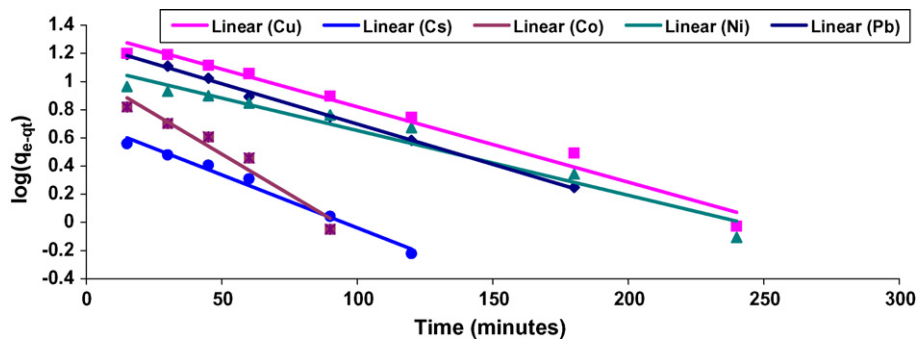


Fig. 3. Lagregren's plot of linearized sorption data for all the studied elements using arca shell biomass.

the optimum dose was observed at 12.5 g/L with variation in the uptake as the initial concentration are different for the elements. Data from the variation of biosorbent doses was fitted for the Freundlich and Langmuir isotherms to estimate the relevant parameters under conditions of limited ions available to active binding sites variations.

### 3.2.4. Effect of initial concentration

Study was carried out concentrations range from 10 to 500 ppm under optimised conditions of pH and contact time with dosages. There was a continuous increase in the uptake of metal per gram of biosorbent up to a concentration 100  $\mu\text{g}/\text{mL}$  for all the four elements except cesium at higher concentrations a slight increase was observed. In case of lead the uptake of 18.33 mg/g was observed from initial concentration of 100 ppm and at higher initial concentration the uptake was increased up to 30.44 mg/g from initial concentration of 500 ppm but the residual concentration in the treated water increased from less than 10 ppm to more than 340 ppm. In this way on the basis of optimum maximum uptake and minimum residual concentration after treatment the initial concentration were optimised. Data from these studies were fitted in the Langmuir and Freundlich isotherm equation to evaluate the relevant parameters.

### 3.2.5. Effect of competitive ions on the sorption

Experiments were conducted under all the optimised conditions of pH, contact time, dose rate and concentration using different concentrations of sodium, potassium, calcium and magnesium individually and in combinations at the varying concentration, e.g. 0, 10, 20, 50, 100, 400 and 500  $\mu\text{g}/\text{mL}$  for

both the elements. Percentage removal of lead decreased from 91.66 to 85.5 in presence of sodium ion concentrations of 0 and 500  $\mu\text{g}/\text{mL}$ , respectively, but effect on the percentage removal up to the concentration of 50  $\mu\text{g}/\text{mL}$  was almost negligible (Fig. 4). The effect of potassium was almost negligible on the lead removal as the removal was decreased by just 3% from 91.66 to 88.08 at 500 ppm of potassium in comparison to sorption in the absence of potassium (Fig. 4). Effect of calcium and magnesium in combination is on higher side as the percentage removal declined to 62.6% at 500 ppm of calcium and magnesium in comparison to 91.66% with out any contamination. In presence of all the four cations the percent removal of lead decreased to 50% from the 91.6% in contamination free lead solutions (Fig. 4). Copper sorption on the arca shell biomass is more sensitive to the presence of the sodium, potassium, calcium and magnesium (Fig. 5). The removal of the copper lowers down to 60.3% in presence of 500 ppm of sodium concentration from 88.2% from the contamination free solution of copper (Fig. 5). The effect of sodium cations of the copper sorption is almost negligible as the percent removal is more than 83% at 500 ppm sodium ions contamination. Presence of both cations sodium and potassium hits the sorption capacity more severely as the percent removal declined to less than half (40.3%). Presence of calcium and magnesium at 500 ppm jointly lower down the percent copper removal from 88.2 to 38.6% (Fig. 5). In presence of all the four cations (Na, K, Ca and Mg) simultaneously the percentage removal comes to just 20.9% from the 88.2% levels of contamination free solutions (Fig. 5). Removal of nickel is also affected by the presence of the common ions like sodium, potassium, calcium and magnesium. Percentage removal of the

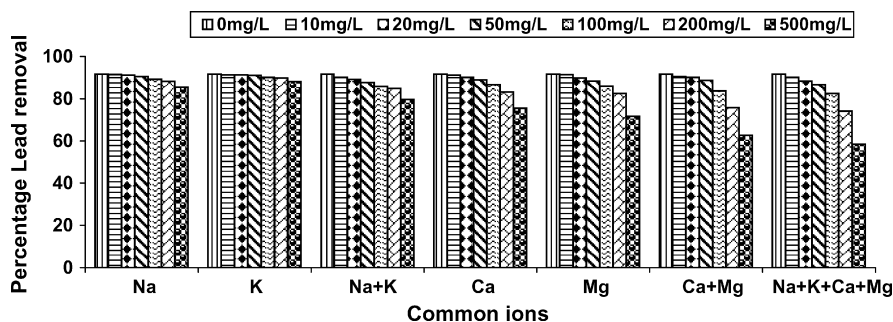


Fig. 4. Effect of common ions on the removal efficiency of lead using arca shell biomass (pH 4.0; contact time = 240 min; initial concentration = 100 ppm and ASB dose = 5.0 g/L).

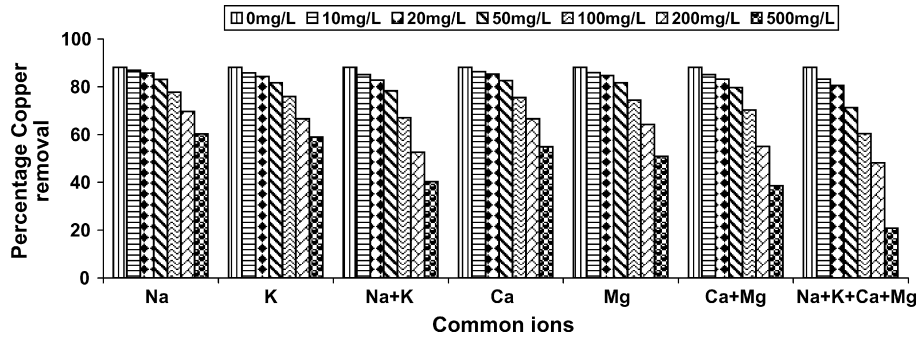


Fig. 5. Effect of common ions on the removal efficiency of copper using arca shell biomass (pH 4.5; contact time = 300 min; initial concentration = 100 ppm and ASB dose = 5.0 g/L).

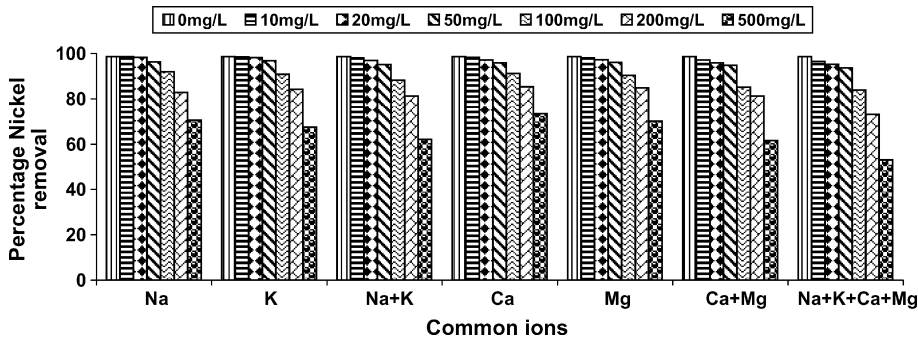


Fig. 6. Effect of common ions on the removal efficiency of nickel using arca shell biomass (pH 5.0; contact time = 300 min; initial concentration = 100 ppm and ASB dose = 10.0 g/L).

nickel declined to 70.6 in presence of 500 ppm of sodium ions in the solution from 98.6% without any cationic inference (Fig. 6). At the same level of contamination of potassium the percentage removal comes down to 67.6% whereas the combined effect of sodium and potassium at same contamination levels lowers down the percentage removal to 62% (Fig. 6). Contamination of all the four cations simultaneously bring down the percentage removal of nickel to 53% which shows less affected in comparison to copper removal but more sensitive to lead removal by using arca shell biomass (Figs. 4–6).

Presence of sodium affects the sorption of cesium and the percentage removal declined to 60.6% at 500 ppm level contamination from 90.8% at 50 ppm and 98.2% from contamination free solutions (Fig. 7). Potassium also showed adverse effect on the sorption mechanism of cesium on arca shell biomass as

the removal comes to 66.7% at 500 ppm potassium ion concentration from 98.2, from contamination free cesium solutions (Fig. 7). In the combination of sodium and potassium the effect is slightly on higher side, but the effect was only at the higher concentration of the competitive ion concentrations. The combined effect of sodium and potassium the percentage removal decreased from 98.2 to 54.6% in the presence of this cation from 0 to 500  $\mu\text{g}/\text{mL}$  (Fig. 7). The effect was negligible up to the concentration of 50  $\mu\text{g}/\text{mL}$  of sodium and potassium (Fig. 7).

The removal decreases from 98.2% in absence of calcium ion to 61.2% at 500  $\mu\text{g}/\text{mL}$  (Fig. 7). In case of magnesium the trend is almost similar to the earlier one. The percentage removal decreases from 98.0 to 53.4% in presence of 10–500  $\mu\text{g}/\text{mL}$  of magnesium (Fig. 7). The effect of calcium and magnesium was almost negligible up to their concentration of 20  $\mu\text{g}/\text{mL}$ . But,

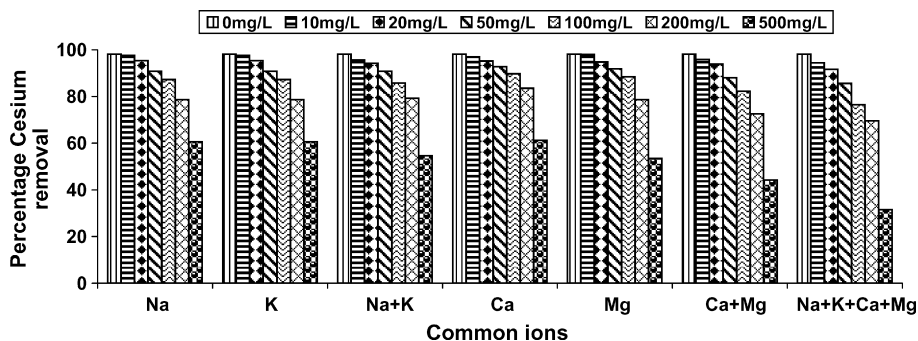


Fig. 7. Effect of common ions on the removal efficiency of cesium using arca shell biomass (pH 5.5; contact time = 180 min; initial concentration = 50 ppm and ASB dose = 12.5 g/L).

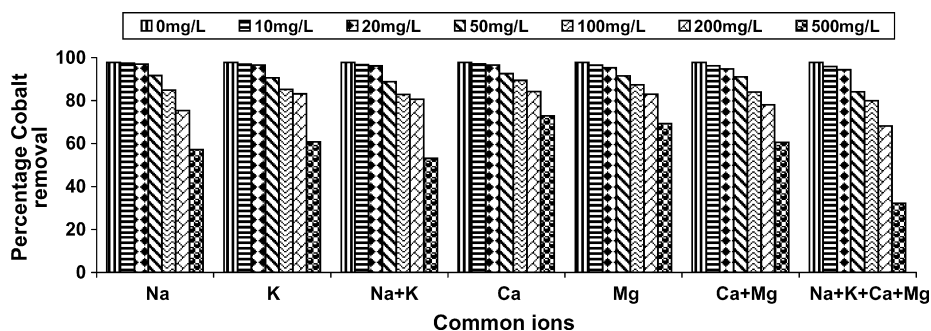


Fig. 8. Effect of common ions on the removal efficiency of cobalt using arca shell biomass (pH 4.0; contact time = 120 min; initial concentration = 100 ppm and ASB dose = 12.5 g/L).

at the concentration of 500  $\mu\text{g}/\text{mL}$  the percentage removal of lead was decreased to 44.2% in comparison to 98.2% in their absence. The combined effect of all the cations was at higher side and the removal was declined to just 31.6% at 500  $\mu\text{g}/\text{mL}$  in comparison to 98.2% in the absence of these cations.

In case of cobalt the removal was decreased from 97.8 to 57.2% the presence of 500  $\mu\text{g}/\text{mL}$  in comparison to the absence of sodium ions (Fig. 8). In case of potassium the percent copper removal decreased to 60.8% at the same concentration level (Fig. 8). The combined effect of sodium and potassium at 500  $\mu\text{g}/\text{mL}$  bring down the cobalt removal to 53.1% in comparison to their absence in the solution (Fig. 8). At the 500  $\mu\text{g}/\text{mL}$  concentration the removal percentage of cobalt decreased to 72.9 and 69.4% for calcium and magnesium, respectively (Fig. 8). The combined effect of calcium and magnesium decreased the cobalt removal to 60.6% in comparison to 96.2% at concentration of 10  $\mu\text{g}/\text{mL}$  of both the cations (Fig. 8). In the presence of all the four cations the percentage removal of cobalt decreased to 32.2% at 500  $\mu\text{g}/\text{mL}$  in comparison to 97.8% in the absence of these cations (Fig. 8).

#### 4. Influence of initial pH

It is well known fact that pH of the medium affects the solubility of the metal ions and the concentration of the counter ions on the functional group of the biomass. pH is one of the most important environmental factor which influences not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and inorganic ligands, redox reactions, and precipitation are strongly influenced by pH and on the other hand, strongly affects the speciation and the biosorption availability of the heavy metal [49,50]. Since pH is one of the main parameter affecting the biosorption process [51]. At low pH, protons would compete with metals for the active sites responsible for the biosorption would have decreased the metal sorption. At low pH, e.g. pH 2 and less all the binding sites may be protonated, thereby even desorbs all the metal bound with biomass [46,52]. An additional possible explanation for increase of sorption at higher pH is that the solubility of many metals in the solution decrease with increasing pH in the range from 3 to 6 is also conformed by the results for all the studied element removal using ASB (Fig. 1). Increase of sorption with pH may be due to the hydrolyzed species having a lower degree

of hydration, i.e. less energy is necessary for removal or reorientation of the hydrated water molecules upon binding [53]. At a further increase of pH (6–9) the solubility of metals decreases enough for precipitation to occur as in present study lead nitrate and copper sulphate precipitation occurs at pH 6 and 6.5, respectively [53]. Arca shell biomass contains ionizable groups, which makes it very liable to the influence of pH. As shown in Fig. 1, percentage removal of all the elements using arca shell biomass depends on pH, increases with pH from 1 to 3 and then reaches a plateau at higher pH due to lower content of ionizable group in the biomass [54–57].

#### 4.1. Kinetics isotherm

The isotherm has been of importance in the wastewater treatment by adsorption technique, as it provides estimation of sorption capacity of the adsorbent. The adsorption data obtained for lead, copper, nickel, cesium and cobalt using arca shell biomass as adsorbent were analyzed using Lagergren, Freundlich and Langmuir equations.

The sorption rate constant was determined ( $k_1 = 0.013 \text{ min}^{-1}$ ) from the slope of the linear plot of  $\log(q_e - q_t)$  versus time resulted in straight line follows the first-order rate kinetics ( $R^2 = 0.976$ ) as per Lagergren equation at room temperature for initial concentration of 100  $\mu\text{g}/\text{mL}$  of lead with a dose of 5.0 g/L as shown in Fig. 3. The coefficient ( $K_L$ ) of Lagergren was 18.63 (Table 3).

In a rapidly stirred batch reactor the adsorbate species are most probably transported from the bulk of the solution to the solid phase through intra-particle transport, which is often the rate limiting step in many sorption processes [58]. The linear plot (Fig. 9) of  $C_e/q_e$  versus  $C_e$  for metal sorption system under the optimised experimental conditions indicates the applicability of Langmuir adsorption isotherm satisfactorily as the coefficient of determination ( $R^2$ ) is more than 0.97 (Table 3) for all the studied heavy metals and radionuclides, consequently suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent in the concentration studied [47]. The values of coefficients ( $a$  and  $b$ ) were determined for all the studied elements from the slope and intercept of the plots given in Fig. 9. The dimensionless parameter, Hall [45] separation factor ( $R_L$ ), which is defined in Eq. (8) was calculated, where  $b$  is Langmuir constant and  $C_0$  is the initial metal concentration.



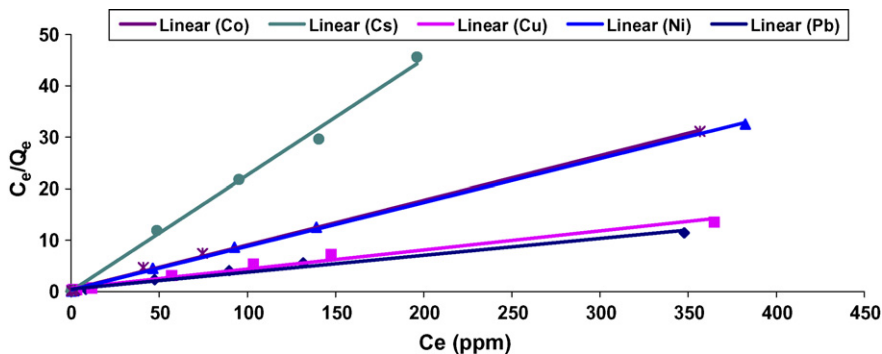


Fig. 9. Langmuir linear fit of batch sorption data for arca shell biomass (constant sorbent dose).

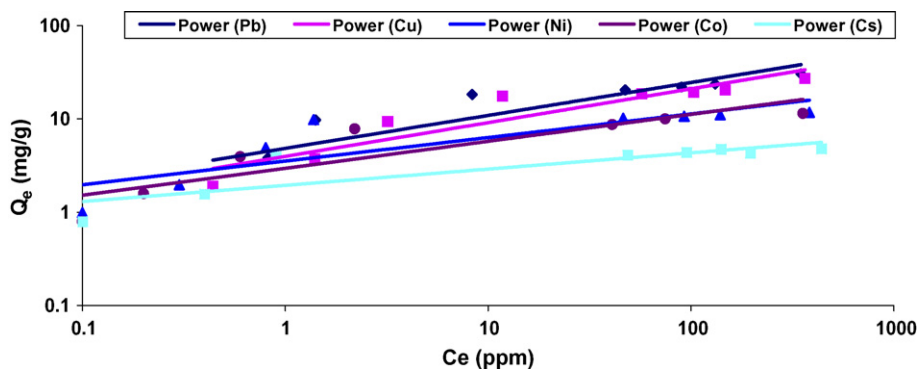


Fig. 10. Freundlich fit of isotherm sorption data for all the studied elements using arca shell biomass (constant biosorbent dose).

If  $R_L$  lies between 0 and 1 indicates the favourable conditions for metal sorption on the sorbent. It was observed that nickel shows the lowest value (0.034) of separation factor followed by cobalt (0.043), cesium (0.083), lead (0.125) and nickel (0.146) indicates the stronger the monolayer adsorption on the adsorbent (Table 3). Free energy changes evaluated for all studied elements are given in Table 3. Free energy change ( $\Delta G$ ) is negative confirming that the sorption processes are spontaneous and exothermic in nature.

The Freundlich model fitting (Fig. 10) was not also found as linear as was observed in case of Langmuir isotherm as indicated by lower values of coefficient of determination ( $R^2$ ) less than 0.86 except cobalt sorption system where it was observed as 0.924 (Table 3). The mechanism rate of adsorption is reported to be the function of  $1/n$  and  $K$  were calculated from the Freundlich plot.  $K$  and  $1/n$  are the measure of sorption capacity and intensity of sorption, respectively. The values of  $1/n$  are less than unity (lead: 0.353; copper: 0.362; nickel: 0.253; cesium: 0.174 and cobalt: 0.251) indicate better adsorption mechanism and formation of relatively stronger bonds between adsorbent and adsorbate. Smaller the value of  $1/n$  indicates better adsorption mechanism and formation of relatively stronger bonds between adsorbent and adsorbate [59].

## 5. Conclusion

The treated arca shell biomass, a waste material from marine environment, was converted into a biosorbent, which exhibit

good sorption for the elements studied. Arca shell shows the highest sorption potential for lead followed by copper, nickel, cobalt and cesium. Adsorption isotherms do not follow the Freundlich isotherm and can be better described by Langmuir and Lagergren isotherm having determination coefficient higher than 0.9 for almost all the elements. Free energy change ( $\Delta G$ ) is negative confirming that the sorption processes are spontaneous and exothermic in nature. Effects of all the common ions studied up to the concentration of 200  $\mu\text{g/mL}$  are negligible for lead, nickel and cobalt, but in case of copper and cesium uptake decreased to 50% of the uptake at 200 ppm of all the cation in comparison to the absence of these common ions. This material can be used for the removal of these elements from the liquid effluent after optimisation of different physico-chemical parameters of the effluent. The treated shell, a waste material from the fishing industry, was converted into a biosorbent, which exhibit good sorption for both these heavy metals and cesium.

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## References

- [1] B.D. Honeyman, P.H. Santsch, Metals in aquatic environment, Environ. Sci. Technol. 22 (1988) 862.

- [2] B.L. Carson, H.V. Ellis, J.L. McCann, Toxicology and Biological Monitoring of Metals in Humans, vol. 71, Lewis Publication, Chelsea, Michigan, 1986, p. 133.
- [3] B.W. Mercer, L.L. Ln Ames Jr., L.B. Sand, F.A. Mumplon (Eds.), Zeolite Ion Exchange in Radioactive Municipal Wastewater Treatment in Natural Zeolites, Occurrence, Properties Use, Pergamon Press, Oxford, 1978, pp. 451–459.
- [4] K.C. Song, H.K. Lee, H. Moon, K.J. Lee, Simultaneous removal of the radiotoxic nuclides  $^{137}\text{Cs}$  &  $^{129}\text{I}$  from aqueous solution, Sep. Purif. Technol. 12 (1997) 215–217.
- [5] International Commission of Radiological Protection Individual Monitoring for Internal Exposure of Worker: Replacement of ICRP Publication 54, Pergamon Press, ICRP Publication, 1998, p. 78.
- [6] R.R. Jalali, H. Ghafourian, Y. Asef, S.T. Dalir, M.H. Sahafipour, B.M. Gharanjik, Biosorption of cesium by native and chemically modified biomass of marine algae: introduce the new biosorbent for biotechnology applications, J. Hazard. Mater. B116 (2004) 125–134.
- [7] E.J. Underwood, Trace Elements in Human and Animal Nutrition, 4th ed., Academic Press, New York, 1977.
- [8] WHO, Health Criteria and Other Supporting Information Guidelines for Drinking Water Quality, vol. II, WHO, Geneva, 1984, p. 126.
- [9] WHO, International Programme on Chemical Safety, Environmental Health Criteria, vol. 108, Geneva, 1991, p. 286.
- [10] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. No'breaga, M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, Process Biochem. 40 (11) (2005) 3485–3490.
- [11] H. Topallar, Y. Bayrak, Investigation of adsorption isotherms of myristic, palmitic and stearic acids on the rice hull ash, Turk. J. Chem. 1 (1999) 193–198.
- [12] M. Al-Qunaibit, M. Khalil, A. Al-Wassil, The effect of solvents on metal ion adsorption by the alga *Chlorella vulgaris*, Chemosphere 60 (2005) 412–418.
- [13] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column, Chemosphere 60 (2005) 419–426.
- [14] K. Chojnacka, Biosorption of Cr(III) ions by eggshells, J. Hazard. Mater. B121 (2005) 167–173.
- [15] O. Gulnaz, S. Saygideger, E. Kusvuran, Study of Cu(II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study, J. Hazard. Mater. B120 (2005) 193–200.
- [16] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2005) 185–192.
- [17] F. Pagnanelli, S. Mainelli, S. De Angelis, L. Toro, Biosorption of protons and heavy metals onto olive pomace: modelling of competition effects, Water Res. 39 (2005) 1639–1651.
- [18] A.S. Bilques, P.P. Sharma, S. Mohammad, Adsorption studies on phosphate treat saw dust: separation of Cr(IV) from  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  and their removal and recovery from electroplating waste, Indian J. Environ. Prot. 19 (11) (1999) 846–852.
- [19] K. Periasamy, C. Namasivayam, Removal of copper(II) by adsorption onto peanut hull carbon from wastewater and copper plating industry wastewater, Chemosphere 32 (1996) 769–789.
- [20] C.R. Nagendra Rao, L.C. Iyenger, Venkobacher, Sorption of Cu(II) from aqueous phase by waste biomass, J. Environ. Eng. 119 (1993) 369–377.
- [21] V. Isabel, M. Maria, M. Nuria, Heavy metal uptake from aqueous solution by Cork and Yohimbe bark wastes, J. Chem. Technol. Biotechnol. 75 (2000) 812–816.
- [22] R. Gong, X. Zhang, H. Liu, Y. Sun, B. Liu, Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel, Bioresour. Technol. 98 (2007) 1319–1323.
- [23] A. Saeed, M.W. Akhter, M. Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Sep. Purif. Technol. 45 (2005) 25–31.
- [24] K. Conrad, H.C.B. Hansen, Sorption of zinc and lead on coir, Bioresour. Technol. 98 (2007) 89–97.
- [25] S. Karthikeyan, R. Balasubramanian, C.S.P. Iyer, Evaluation of the marine algae *Ulva fasciata* and *Sargassum* sp. for the biosorption of Cu(II) from aqueous solutions, Bioresour. Technol. 98 (2007) 452–455.
- [26] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.
- [27] K. Vijayaraghavan, K. Palanivelu, M. Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, Bioresour. Technol. 97 (2006) 1411–1419.
- [28] M.Y. Can, Y. Kaya, O.F. Algur, Response surface optimization of the removal of nickel from aqueous solution by cone biomass of *Pinus sylvestris*, Bioresour. Technol. 97 (2006) 1761–1765.
- [29] T. Akar, S. Tunali, Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution, Bioresour. Technol. 97 (2006) 1780–1787.
- [30] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Ternary biosorption studies of Cd(II), Cr(III) and Ni(II) on shelled *Moringa oleifera* seeds, Bioresour. Technol. 98 (2007) 474–477.
- [31] Y. Pamukoglu, F. Kargi, Biosorption of copper(II) ions onto powdered waste sludge in a completely mixed fed-batch reactor: estimation of design parameters, Bioresour. Technol. 98 (2007) 1155–1162.
- [32] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using Eucalyptus bark, Bioresour. Technol. 97 (2006) 15–20.
- [33] S. Dahiya, U. Mehta, A.G. Hegde, R.P. Gurg, Studies on sorption potential of chemically activated sugarcane bagasse carbon for cesium removal from aqueous solution, Radiat. Prot. Environ. 26 (2003) 468–472.
- [34] S. Dahiya, D.G. Mishra, R. Karpe, A.G. Hegde, R.P. Gurg, Removal of lead and copper from aqueous solution by using chemically activated sugarcane bagasse carbon, Natl. Symp. Environ. Proc. 12 (2003) 400–406.
- [35] S. Dahiya, R.M. Tripathi, M. Saini, A.G. Hegde, Sorption of lead and copper from aqueous solutions by pre-treated marine algae biomass, Natl. Conf. Recent Trends Surface Chem. (2005) 14–15.
- [36] S. Dahiya, R.M. Tripathi, S. Singh, A.G. Hegde, Sorption of lead and copper from aqueous solutions by pre-treated mangroves roots biomass, Environ. Geochem. 8 (1/2) (2005) 349–355.
- [37] P.R. Sangurdekar, J.S. Melo, S.F. D'Souza, Biosorption of radioactive cobalt and cesium using mucilaginous seeds, Proc. Natl. Symp. Environ. (2001) 298–299.
- [38] J.S. Melo, S.F. D'Souza, Biosorption of uranium and thorium by agro based biomass, Natl. Symp. Environ. (2001) 293–296.
- [39] F. Veglio, F. Beolchini, Removal of metal by biosorption—a review, Hydrometallurgy 44 (1997) 301–316.
- [40] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
- [41] B. Benguella, H. Benaissa, Cadmium removal from aqueous solution by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.
- [42] Z. Aksu, Equilibrium and kinetic modeling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.
- [43] J.J. Kipling, Adsorption from Solutions of Nonelectrolytes, Academic Press, London, 1965, pp. 113, 259.
- [44] G.D. Parfitt, C.H. Rochester (Eds.), Adsorption from Solution at Solid/Liquid Interface, Academic Press Inc., London, 1983, pp. 7, 42.
- [45] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vemeulen, Pore and solid diffusion in fixed bed adsorption under constant pattern condition, Ind. Eng. Chem. Fundam. 5 (1966) 213–223.
- [46] R. Gupta, P. Ahuja, S. Khan, R.K. Sexena, H. Mohapatra, Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions, Curr. Sci. 78 (2000) 967–973.
- [47] K.K. Pandey, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, Water Res. 19 (1985) 869–873.
- [48] M.R. Ferguson, T.M. Peterson, A. Jeffers, in: B.J. Scheiver, F.M. Doyle, S.K. Kawatra (Eds.), Proceedings of 1989 SME Symposium on Biotechnology in Minerals and Metal Processing, vol. 24, SME, 1989, pp. 201–207.
- [49] A. Casas, F. Alvarez, L. Cifuentes, Aqueous speciation of sulphuric acid–cupric sulphate solutions, Chem. Eng Sci. 55 (2000) 6223–6234.
- [50] M.U. Corapcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, Water Res. 21 (9) (1987) 1031–1044.

- [51] J.M. Lezcano, F. Gonzalez, I. Perez, M.L. Blazquez, J.A. Munoz, A. Ballester, A. Hammami, Use of waste biomass for decontamination of liquid effluents by biosorption., *Bio-hydrometall.: Fundam. Technol. Sustainable Dev. Part B* (2001) 217–226.
- [52] I. Aldor, E. Fourest, B. Volesky, Desorption of cadmium from algal biosorbent, *Can. J. Chem. Eng.* 73 (1995) 516–522.
- [53] S. Schiewer, B. Volesky, Modeling of the proton-metal ion exchange in biosorption, *Environ. Sci. Technol.* 29 (1995) 3049–3058.
- [54] Y. Sag, A. Kaya, T. Kutsal, The simultaneous biosorption of Cd(II) and Zn(II) on *Rhizopus arrhizus*: application of the adsorption models, *Hydrometallurgy* 50 (1998) 297–314.
- [55] J.L. Zhou, P.L. Huang, R.G. Lin, Sorption and desorption of Cu and Cd by macroalgae and microalgae, *Environ. Pollut.* 101 (1998) 67–75.
- [56] J.T. Matheickal, Q. Yu, Biosorption of lead (II) and copper(II) from aqueous solution by pre-treated biomass of Australian marine algae, *Bioresour. Technol.* 69 (1999) 223–229.
- [57] W.M. Antunes, A.S. Luna, C.A. Henriques, A.C.A. da Costa, An evaluation of copper biosorption by a brown seaweed under optimized conditions, *Electron. J. Biotechnol.* 6 (3) (2003) 174–184.
- [58] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solutions, *J. Sanit. Eng. Div.* 18 (1963) 31–59.
- [59] S.D. Faust, M.A. Osman, *Adsorption Process for Water Treatment*, Butterworths, London, 1987, p. 15.
- [60] R.E. Treybal, *Mass Transfer Operations*, 3rd ed., McGraw Hill, New York, 1980, pp. 447–522.
- [61] B. Volesky, Detoxification of metal bearing effluents: biosorption for next century, *Hydrometallurgy* 59 (2001) 203–216.